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SELECTION OF STRUCTURAL PARAMETERS IN DEVELOPING CHEMICAL COMPOSITIONS FOR GLASS MICROSPHERES

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The author analyzes certain parameters determining the structure of glasses, which ought to be taken into account in developing chemical compositions for microspheres, namely, the molar volume, the silicate modulus (for silicate glasses), the gas permeability coefficient, and the structure coherence factor. Furthermore, the parameter of internal porosity is proposed.

Glass microspheres used as hydrogen containers should have high resistance to atmospheric effects and low gas permeability. There are no known methods for designing glass-forming mixtures that would simultaneously satisfy the above requirements [1, 2]; these requirements are mutually exclusive, considering that chemical resistance increases as the content of glass-forming oxides (SiO_2 , GeO_2 , and Al_2O_3 [1, 3]) grows, but gas permeability in this case increases as well. Below are corroborating data on the penetration of helium through various glasses at a temperature of 300°C [4].

Glass	Helium penetration coefficient, $\text{m}^3 \cdot \text{m}/(\text{m}^2 \cdot \text{sec} \cdot \text{Pa})$
Quartz	23.70×10^{-18}
Pyrex	2.86×10^{-18}
Soda-lime.	7.37×10^{-20}
Lead	2.78×10^{-20}
Jena.	2.70×10^{-20}
Thuringian	6.32×10^{-21}

The gas permeability coefficient K is found from the following formula:

$$K = \frac{qd}{A\tau(P_2 - P_1)}, \quad (1)$$

where q is the total gas flow via glass, m^3 ; A is the surface area of glass, m^2 ; τ is the process duration, sec; $(P_2 - P_1)$ is the difference in partial pressures of diffusing gas on both sides of the glass, Pa; d is the glass thickness, m.

It can be seen that quartz glass consisting of 100% SiO_2 has the highest gas permeability, and the gas permeability of

Thuringie glass bearing up to 12% Na_2O [5] is the lowest, probably, due to Na_2O . The effect of the chemical composition is not taken into account in formula (1). This is typical of various studies of this kind.

It is reported in [5] that the permeability of quartz glass and vitreous boric anhydride decreases when sodium, potassium, and other cations are introduced into the system. It is stated that the higher the sodium content, the lower the helium permeability of glass at 300°C. However, it is well known in glass technology that alkaline metal oxides degrade the chemical resistance of glasses [3].

The qualitative effect of the composition is accounted for in [5] in the following way. Permeability is an indicative function of the Na_2O content, and at the same time it characterizes the packing density of the glass structure. Small ions (Li^+) decrease permeability, whereas large ions (Na^+) enhance it. Taking into account ion diffusion, it is noted that gas permeability is affected by the relative mobility and polarizing force of cations, which is observed in the small Li^+ cations. The relative packing density index, which is proportional to the volume of ions and inversely proportional to the absolute volume depending on molar weight and density, is regarded as the measure of gas permeability. The formula of the relationship between permeability and chemical composition is not supplied, but it is observed that the index can be applied when glass contains only univalent cations of alkaline metals and the structure is based on the silicon-oxygen skeleton.

The problem of selecting an appropriate chemical composition is complicated by extremely scarce data on the dependence of hydrogen permeability on the content of microsphere-glass components, which could serve as the basis for establishing a reliable mathematical expression of such a dependence.

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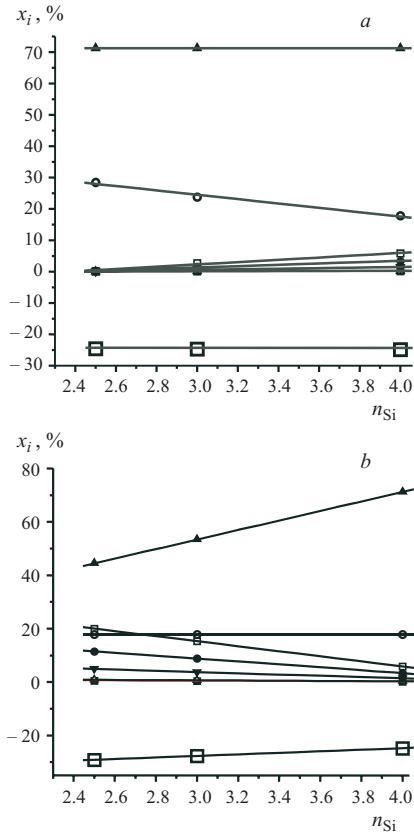


Fig. 1. Variation of the molar content x_i of oxides in hypothetical compositions with a constant content of SiO_2 (a) and Na_2O (b) and the logarithm of hydrogen permeability coefficient $\log K$ as a function of silicate modulus n_{Si} : \blacksquare K_2O ; \square CaO ; \bullet MgO ; \circ Na_2O ; \blacktriangle SiO_2 ; \triangle Al_2O_3 ; \blacktriangledown B_2O_3 ; \square $\log K$.

The study in [6] contains a mathematical expression of the relationship between the chemical composition and hydrogen permeability of glass [mole \cdot m/($m^2 \cdot$ sec \cdot Pa)]:

$$K_{H_2/sec} = 8.1 \times 10^{-14} \exp\left(-\frac{17,330 - 127.8G}{T}\right), \quad (2)$$

where T is the temperature, K , and G is the molar content of glass-forming oxides ($SiO_2 + B_2O_3 + P_2O_5$), %.

The obvious drawback of the formula is the fact that it does not take into account the content of other glass components (intermediate oxides and modifiers), as well as the capacity of cations for changing the oxygen coordinate number: in some cases this consolidates the structure and in others loosens it, which is reflected in the gas permeability. This can be illustrated by the example in [5]: Na_2O and B_2O_3 consolidate the glass structure, whereas the same quantity of SiO_2 additive loosens the structure. These effects in mixed boron-silicate glasses oppose each other; therefore, there should exist a certain value of optimum density. This optimum is accomplished when the weight content of B_2O_3 in sodium-boron-silicate glass is equal to 18%. The anomaly is determined by the joint effect of B_2O_3 and the cation Na^+ , which modifies oxygen coordination of boron in glasses. Such anomalies do not exist in alkali-free glasses.

It should be noted that the opinions of the authors in [5] and [6] regarding the effect of glass components on gas permeability disagree: the authors in [5] refer to alkaline oxides, and those in [6] concentrate only on glass-forming oxides,

Let us analyze several hypothetical glass-forming compositions (Table 1). The hydrogen permeability coefficient was calculated based on formula (2), and the molar volume of oxides was determined using the method described in [2].

It can be seen from Table 1 that in the first case the constant value was the SiO_2 volume, and in the second case the Na_2O volume. The overall molar volumes of the components $\Sigma \log V_i$ (without taking into account Na_2O and SiO_2 volumes) in these cases were, respectively, 0.07 – 2.34 and 2.34 – 8.02 cm^3 /mole, the respective silicate moduli n_{Si} did not vary (4.0, 3.0, and 2.5), and the logarithm of the hydrogen permeability coefficient $\log K$ in the first case virtually did not vary, i.e., by appearance no structural modifications occurred and the glass permeability did not change when the glass composition varied. This is a logical contradiction that has to be rejected. The dependences $\log V_i = f(n_{Si})$ in the graphical shape are shown in Fig. 1.

Thus, formula (2) is the result of one of a few attempts at a quantitative description of the correlation between hydrogen permeability and the chemical composition, which constitutes its main virtue. The formula does not reflect the relationship between gas permeability and structural modifica-

TABLE 1

Silicate modulus	Logarithm of total molar volume of oxides in glass structure [cm ³ /mole]	Molar content, %							Logarithms of hydrogen permeability coefficient [mole \cdot m/(m ² \cdot sec \cdot Pa)]
		K ₂ O	CaO	MgO	Na ₂ O	SiO ₂	Al ₂ O ₃	B ₂ O ₃	
4.0	2.34	0.136	5.83	3.35	17.80	71.22	0.24	1.42	– 24.82
3.0	1.07	0.062	2.68	1.54	23.74	71.22	0.11	0.65	– 24.96
2.5	0.07	0.004	0.16	0.09	28.49	71.22	0.01	0.04	– 25.08
4.0	2.34	0.136	5.84	3.35	17.80	71.22	0.24	1.42	– 24.82
3.0	6.13	0.357	15.30	8.77	17.80	53.42	0.62	3.72	– 27.71
2.5	8.02	0.467	20.04	11.49	17.80	44.51	0.82	4.87	– 29.15

tions in glass; however, formula (2) can be used for understanding the trend in the variation in gas permeability when the glass composition is modified.

Consequently, there have been no mathematical expressions uniquely suitable for quantitative calculations in designing glass compositions for microspheres, taking into account gas permeability, except for formula (2).

The purpose of our study consisted of analyzing the structural characteristics of glasses and selecting basic parameters in the development of chemical compositions for glass microspheres to serve as gas microballoons.

For many years the two-component system $\text{Na}_2\text{O} - \text{SiO}_2$ has been the basis of microsphere production. The structure of alkaline-silicate glass is determined by the silicate modulus, since it determines the synthesis of the main crystalline phases. The silicate modulus is equal to the ratio of SiO_2 and Na_2O content [7]:

$$n_{\text{Si}} = [\text{SiO}_2]/[\text{Na}_2\text{O}],$$

where $[\text{SiO}_2]$ and $[\text{Na}_2\text{O}]$ are the molar contents of oxides, %.

It is established that an identical silicate modulus of glass-forming compositions does not mean an identical parameter of hydrogen permeability. Therefore, the silicate modulus is a necessary but not a sufficient parameter in designing glass-forming solutions. Another criterion should be the hydrogen permeability coefficient [6], despite its insufficient correctness.

The glass structure to a great extent depends on the coordination state of the cations. This determines the configuration of coordination polyhedrons, which in the aggregate form structural fragments. The factor Y suggested by N. N. Ermolenko [8] can be used to characterize the coherence (the degree of branching) of the structural skeleton. The coherence factor Y is the average number of bridge bonds or bridge oxygen atoms in structural polyhedrons. Its value can vary from 2 to 4. With $Y=4$, a three-dimensional skeleton is formed produced by 4 bridge bonds per glass-forming cation; a two-dimensional laminar skeleton is formed with $Y=3$, and a one-dimensional chain structure arises with $Y=2$. If $Y<2$, the formation of glass is impossible. The study in [8] describes the respective structural fragments and suggests a calculation formula:

$$Y = \frac{\sum I_i z_i - \sum I_j}{\sum I_i},$$

where $\sum I_i$ and $\sum I_j$ are the sum of atoms with the number of bonds more than one and equal to one, respectively; z_i is the valence or coordination number.

In calculating the Y factor based on the composition, one uses their concentration expressions $\sum n[i]$ instead of $\sum I_i$ and $\sum I_j$ (n is the number of metal atoms in the respective oxide molecule i).

The advantage of the factor Y is the fact that it determines the relationship between the quantitative ratios of the glass components or the coordination state of the cations and the arrangement of the structural fragments.

The structural characteristics should include partial \bar{V}_i and molar V_i volumes of ingredient oxides (cm^3/mole). The calculation method is described in [2]:

$$\bar{V}_{\text{SiO}_2} = 26.1 + 0.035([\text{SiO}_2] - 67);$$

$$\bar{V}_{\text{B}_2\text{O}_3} = 21.0 + 0.08([\text{SiO}_2] + [\text{B}_2\text{O}_3] - 50),$$

where $[\text{SiO}_2]$ and $[\text{B}_2\text{O}_3]$ are the molar contents of oxides, %.

The value $\bar{V}_{\text{B}_2\text{O}_3}$ is calculated based on the quantity of SiO_2 and the ratio of the molar content of metal oxides and boric anhydride Ψ . If $[\text{SiO}_2] < 71\%$, then $\bar{V}_{\text{B}_2\text{O}_3} = 18.5$ at $\Psi > 4$, $\bar{V}_{\text{B}_2\text{O}_3} = 18.5 + 3.1 \times (4 - \Psi)$ at $4 > \Psi > 1$, $\bar{V}_{\text{B}_2\text{O}_3} = 34.0 - 3.1 \times \left(3 - \frac{1}{\Psi}\right)$ at $1 > \Psi > \frac{1}{3}$, and $\bar{V}_{\text{B}_2\text{O}_3} = 36.0$ at $\Psi < \frac{1}{3}$. The partial volumes for other oxides are indicated in [2].

The molar volumes are calculated based on the general formula

$$V_i = \bar{V}_i m_i,$$

where m_i is the molar part of the respective oxide.

Another parameter can be considered, namely, internal porosity P_{int} . Let us assume that the material structure consists of 100% SiO_2 . If SiO_2 is removed, a 100% vacancy is formed, which can be filled by other oxides. The introduced oxides cannot fill the entire vacant space, since absolutely poreless materials do not exist. Let us regard the free space of the structural volume as internal porosity P_{int} and express it as percentage. The P_{int} parameter can be used to estimate the number of moles of gas (hydrogen) existing inside the structural cavities of a vitreous material and diffusing beyond the boundaries of the structure in a certain time:

$$P_{\text{int}} = 100 \frac{V_{\text{Si}} - \sum V_i}{V_{\text{Si}}} = 100 \left(1 - \frac{\sum V_i}{V_{\text{Si}}}\right).$$

The expression $\left(1 - \frac{\sum V_i}{V_{\text{Si}}}\right)$ indicates which part of the

structural volume becomes filled by oxides after they are added to the composition. In this case:

$$V = 0.01 P_{\text{int}} m_g / \rho_g,$$

where V is the free-space volume in glass, which is evidently expressed in volume units and not in percent, in contrast to P_{int} ; 0.01 is the coefficient of conversion from percentage to fraction of unity; m_g and ρ_g are the weight and the density of glass, respectively.

In the case of microspheres, whose wall thickness is $1 - 20 \mu\text{m}$, sealed porosity can be assumed as nonexistent; then V is the sum of open pores. The weight and the density of the glass are calculated according to the method in [2] based on the chemical composition or are found empirically.

The number of molecules of a gaseous material in a volume unit is expressed by the Loschmidt number N_L and under normal conditions is equal to $2.6868 \times 10^{25} \text{ m}^{-3}$ [9]. Then the number of gas molecules N_{gas} in the volume will be as follows:

$$N_{\text{gas}} = V N_L.$$

The Avogadro number N_A expresses the number of molecules per mole of gaseous material and is equal to $6.022 \times 10^{23} \text{ mole}^{-1}$ [9]. Accordingly, one can find the number of gas moles μ contained in the volume and capable of diffusion via the sphere wall:

$$\mu = \frac{N_{\text{gas}}}{N_A} \text{ or } \mu = \frac{V N_L}{N_A}.$$

After simple transformations we obtain the following expression:

$$\mu = 0.45 \times 10^2 \frac{m_g}{\rho_g} \left(1 - \frac{\sum V_i}{V_{\text{Si}}} \right). \quad (3)$$

The ratio m_g/ρ_g is the volume of the glass shell of the microsphere, which can be calculated from the formula

$$V_g = 4\pi \frac{d_{\text{ext}}^3 - d_{\text{inn}}^3}{3},$$

where d_{ext} and d_{inn} are, respectively, the external diameter of the microsphere and the diameter of its inner cavity, which are fairly easy to measure.

By designating $V_g \times 0.45 \times 10^2$ with the constant k , expression (3) is written as follows:

$$\mu = k \left(1 - \frac{\sum V_i}{V_{\text{Si}}} \right). \quad (4)$$

It follows from formula (4) that the capacity of glass for absorbing and retaining gas in its structure depends on the molar volumes occupied by oxides in the glass structure or, more precisely, on the ratio between the molar volumes of the glass-forming oxides and all other oxides.

Evidently, $\left(1 - \frac{\sum V_i}{V_{\text{Si}}} \right) = 0$ at $\sum V_i = V_{\text{Si}}$. This means that gas does not diffuse through the glass, since the ratio of quantities of the modifiers and glass-forming oxides is $50 : 50$, and $V_{\text{int}} = 0$. This does not happen in real life, although one should aspire toward obtaining glass with the minimum possible amount of pores in producing microspheres used as gas containers.

With $\sum V_i = 0$, $\left(1 - \frac{\sum V_i}{V_{\text{Si}}} \right) = 1$, i.e., the gas diffusion via

glass is at a maximum. This is possible when the glass consists of 100% glass-forming agents.

The difference $\left(1 - \frac{\sum V_i}{V_{\text{Si}}} \right) < 0$ will have a meaning if

the direction of diffusion and the sign of the pressure difference inside and outside the microsphere are respectively determined, i.e., it is determined whether gas is flowing from the sphere or the sphere is being filled with gas:

$$0 \leq 1 - \frac{\sum V_i}{V_{\text{Si}}} < 1 \text{ for } 0 < \sum V_i \leq V_{\text{Si}}. \quad (5)$$

It follows from condition (5) that the gas permeability of glass can be controlled by varying the molar volume occupied by oxides in the structure of the glass-forming material. The total molar volume of the modifier oxides and intermediary oxides should not exceed the total molar volume of the glass-forming oxides.

Thus, the concept of "molar volume" should be used as the basic concept in developing glass-forming compositions for glass microspheres used as gas microballoons. This parameter is more informative than the component concentration in evaluating structural specifics of the glass-forming material and, accordingly, its hydrogen permeability. The calculation parameters should include the silicate modulus (for silicate glasses), the gas permeability coefficient, the structure coherence factor, and the internal porosity.

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